Titration of a Weak Acid

Pre-Laboratory Reading: Section 16.3 in Olmstead and Williams, General Chemistry

Purpose: The identity and concentration of an unknown weak acid is determined by titration with standardized NaOH solution.

Introduction

The reaction of an acid and a base is a neutralization reaction. The technique of accurately measuring the volume of solution, such as a strong base, required to react with another reagent, such as a weak acid, is termed a titration. The neutralization titration in this experiment is the reaction of an unknown weak acid, HA, with NaOH:

\[
HA\text{ (aq)} + OH^-\text{ (aq)} \rightarrow A^-\text{ (aq)} + H_2O
\] (1)

An acid-base titration can be monitored either through the use of an acid-base indicator or through the use of a pH meter. Monitoring the pH during titration of a weak acid with a strong base leads to a titration curve, Figure 1. The equivalence point occurs when enough base has been added to react completely with all of the weak acid originally in solution. As can be seen in equation (1), the predominant species in solution at the equivalence point is the conjugate base \(A^-\). This conjugate base reacts with water to give a basic solution at the equivalence point:

\[
A^-\text{ (aq)} + H_2O \rightleftharpoons HA\text{ (aq)} + OH^-\text{ (aq)}
\] (2)

For a weak acid, the pH is not neutral at the equivalence point but is greater than 7.0. The equivalence point can be found as the steepest portion of the titration curve as seen in Figure 1. At the equivalence point, the moles of strong base added is equal to the moles of weak acid being titrated:

\[
M_tV_t = M_xV_x
\] (3)

where \(M_t\) is the concentration of the titrant, \(V_t\) is the volume of added titrant, \(M_x\) is the concentration of the unknown weak acid, and \(V_x\) is the volume of the weak acid that is titrated.

Figure 1. Titration of a weak acid with strong base, NaOH.
The equivalence point (or the end point) of the titration can be estimated visually, as in Figure 1. A more accurate approach is to calculate the derivative (d pH/dV) of the titration curve and plot this function versus volume of added base. As shown in Figure 2, the derivative plot exhibits a clear maximum at the equivalence point.

The derivative of the titration curve is approximated by the finite differences:

\[
\frac{d \text{pH}}{dV} \approx \frac{\Delta \text{pH}}{\Delta V} = \frac{\text{pH}_2 - \text{pH}_1}{V_2 - V_1}
\]  

(4)

where pH\(_1\) is the measured pH at added volume V\(_1\) and pH\(_2\) is the measured pH at added volume V\(_2\). The derivative is calculated with successive pairs of data points, Table 1.

Table 1: Calculation of the derivative of an example titration curve.

<table>
<thead>
<tr>
<th>V (mL) NaOH</th>
<th>pH</th>
<th>ΔpH/ΔV</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.32</td>
<td>3.86</td>
<td>0.5</td>
</tr>
<tr>
<td>10.44</td>
<td>3.92</td>
<td>0.83</td>
</tr>
<tr>
<td>10.56</td>
<td>4.02</td>
<td>1.25</td>
</tr>
<tr>
<td>10.68</td>
<td>4.17</td>
<td>2.58 (equivalence point)</td>
</tr>
<tr>
<td>10.80</td>
<td>4.48</td>
<td>1.58</td>
</tr>
<tr>
<td>10.92</td>
<td>4.67</td>
<td></td>
</tr>
</tbody>
</table>

Another significant volume during a titration is when the number of moles of acid (HA) remaining is exactly equal to the number of moles of conjugate base (A\(^-\)) produced. This point is called the “half-equivalence point” because it occurs when exactly half the weak acid has been titrated. From the Henderson-Hasselbalch equation (5), the half-equivalence point gives pH = pK\(_a\).

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[A^-]}{[HA]} \right)
\]  

(5)
Preparation of Standardized 0.10 M NaOH

A solution of NaOH with accurately determined concentration is used as the titrant in this experiment. Solutions of NaOH readily absorb CO₂ from the atmosphere:

\[
\text{CO}_2 (g) + 2 \text{OH}^- (aq) \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} (l) \quad (6)
\]

This reaction changes the concentration of the hydroxide, so precautions are necessary to minimize the effect. The formation of \( \text{CO}_3^{2-} \) ions in the solution also interferes with the equivalence point, by decreasing the slope of the titration curve at the equivalence point. Solutions must be kept covered while in use and tightly stoppered in storage. The absorption of CO₂ must also be avoided when preparing the solution. Solutions of sodium hydroxide slowly attack glass containers and cause glass stoppers to become stuck. Thus, sodium hydroxide solutions are usually stored in polyethylene bottles. Also, burettes or titration pumps must be thoroughly cleaned immediately after use.

Primary Standards

Laboratory work frequently involves the use of a standardized solution, which is a solution of accurately known concentration. You will use a standardized solution of NaOH for the titration of a weak acid. The concentration is roughly 0.10 M, but the concentration will be determined to better than three-significant figures. The concentration of the NaOH solution is determined by titration against a primary standard. For a substance to be a primary standard, the following criteria should be met. A primary standard substance should be:

- Available in very pure form
- Reasonably soluble
- Stable in the pure form and in solution
- Nonhygroscopic (doesn’t absorb water from the air) and easily dried
- A compound with a reasonably high formula weight

Few substances meet these criteria, so the number of useful primary standards is quite limited. Two common primary standard bases are pure sodium carbonate and borax. The primary standard acid in this experiment is KHP, which is the monoprotic potassium salt of a diprotic carboxylic acid, \( \text{KHC}_8\text{H}_4\text{O}_4 \):

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{K}^+ \\
\text{H} & \\
\text{H} & \\
\text{H} & \\
\text{H} & \\
\end{align*}
\]

The accurate concentration of your sodium hydroxide solution is determined by titration of accurately known masses of KHP. The reaction for the standardization titration is:

\[
\text{KHC}_8\text{H}_4\text{O}_4 (aq) + \text{NaOH (aq)} \rightarrow \text{KNaC}_8\text{H}_4\text{O}_4 (aq) + \text{H}_2\text{O}(l) \quad (7)
\]
To determine the exact concentration of the sodium hydroxide solution, the number of moles of sodium hydroxide that react completely with the known number of moles of KHP is calculated. The number of moles of KHP is equal to the number of moles of added base at the equivalence point: \( M_t V_t = \text{moles KHP} \), where \( M_t \) is the concentration of the titrant and \( V_t \) is the volume of added titrant. You then use this standardized NaOH solution for the titration of the weak acid in Part E of this lab.

**Summary of Experiment**

- Standardize a solution of NaOH with the primary standard KHP to determine the exact concentration of NaOH.
- Use the standardized NaOH solution to titrate the unknown weak acid to determine its identity and concentration. The list of possible weak acids will be provided in the laboratory.
- Next week you will investigate the properties of buffers and then use your weak acid and NaOH to produce a buffer.

**Experimental Procedure**

You will use an automated titration system to perform the titrations, Figure 3. A precision pump replaces the burette used in traditional titrations. A computer controls the pump to deliver titrant in pulses to the reaction vessel. A pH meter is used to measure the pH, and the data are recorded by computer for display and analysis. The data acquisition computer program is Logger Pro, which you have used several times in previous labs. The software is set to record the pH and the derivative of the pH with respect to volume. Detailed instructions for using the automated titration system will be provided in the laboratory.

![Diagram of automated titration setup](image)

Figure 3. The automated titration system is based on a computer controlled titration pump. The progress of the titration is monitored using a pH electrode.

You will perform at least **three standardization titrations of ~0.10 M NaOH**. For this laboratory exercise, you should obtain a relative standard deviation of the concentrations from
the three titrations less than 2%. If the relative standard deviation is too high, more titration trials must be performed to achieve less than 2% relative standard deviation.

**Notes:** If you have an obvious experimental error and need to repeat a trial, you may reject the trial. For example an obvious error is you know that you spilled some KHP. However, if you simply have large errors and are doing multiple titrations, you must include all the titrations in the data analysis. If you think there is an outlier, a quality statistical test (Q-test) can be performed to determine if questionable point is a valid data point or if the data point can be rejected (check with your lab instructor to do a Q-test).

**Part A- Standardization of the Pump (in pairs)**

1. Place the inlet tube of the titration pump into 0.100 M NaOH solution. To flush out any water remaining from the previous use of the titration pump, use the calibration application within Logger Pro to transfer 120 pulses of 0.100 M NaOH to a waste beaker. Determine the mass of a weighing bottle and cap to the nearest 0.1 mg. Transfer 60 pulses of NaOH solution to the weighing bottle, cap, and weigh to the nearest 0.1 mg. Record each weight. Repeat the addition of two more sets of 60 pulses, weighing at the end of each set. The density of 0.100 M NaOH at 20°C is 1.0045 g mL⁻¹. Determine the average volume per pulse and the standard deviation of the trials. The standard deviation of the trials should be less than or equal to 1.0%.

**Part B- Calibrate the pH Electrode (in pairs)**

1. Calibrate the pH electrode using pH 7 and pH 4 buffers using the instructions provided in the laboratory.

**Part C- Standardization of NaOH of Unknown Concentration (in pairs)**

1. Open the automatic titration method file in Logger Pro. Enter the average pulse volume into the heading for the Volume variable, using the instructions provided in the laboratory. Carefully transfer about 0.065 to 0.070 grams of dry KHP (potassium hydrogen phthalate) into a tared, clean, labeled 150-mL beaker. Record the weight to the nearest 0.1 milligram. Prepare three such samples.

3. Dissolve each sample in about 50 mL of deionized water. Place the first sample on the magnetic stirrer. Add a stir bar. Position the pH electrode in the beaker so that the stir bar doesn’t strike the electrode. Check that the reference junction of the pH electrode is submerged. Stir vigorously, but without splashing. Tape the outlet of the titration pump to the side of the beaker with the tip of the delivery tube below the surface of the solution. Use a wash bottle to wash down the sides of the beaker and the pH electrode to make sure all the sample is transferred into the solution.

4. Titrate until the equivalence point has been passed. Save the data file. Determine the volume at the equivalence point from the maximum of the derivative of the pH with respect to volume. Rinse the pH electrode in deionized water. Wipe the outside of the outlet tube from the titration pump with a paper towel to avoid transfer to the next sample.

5. Repeat the titration with the other two samples of KHP.

6. Perform the following calculations to determine whether you need to do another titration.
• Calculate the concentration (mol/L) of NaOH for each of your 3 trials. (Excel is handy for this task.)
• Calculate the average concentration of NaOH, the standard deviation of the trials, and the relative standard deviation. If the relative standard deviation of the trials is greater than 2%, perform a couple more trials to obtain less than 2% error. You must check with your instructor to ensure you have successfully completed the titrations. Once your instructor checks your work, you may continue.

Part D- Calibrate a 1000 µL auto-pipettor (each student)

1. On an analytical balance tare a small beaker (50 mL or smaller) to give zero mass. Add 1000 µL of deionized water to the beaker using an auto-pipettor. Record the weight to 0.1 mg. Tare the beaker and water and add a second 1000 µL volume, record the weight. Repeat this process until you have four trials. The density of water at 20°C is 0.9982 g mL⁻¹. Determine the volume delivered and the standard deviation. The relative standard deviation should be less than 1.0%. If the standard deviation is greater than or equal to 1.0%, repeat the volume calibration.

Part E- Titration of Unknown Weak Acid with Standardized NaOH (each student for the same unknown)

Each student should perform a titration of an unknown weak acid with the standardized NaOH solution from Part C. Determine the pKₐ of this acid by the half-equivalence point of the titration and the concentration of the acid by the equivalence point using the following steps:

1. Add 2.000 mL of the unknown weak acid to a clean (but not necessarily dry) 150-mL beaker. Add 50 mL of water to cover the reference junction of the pH electrode.
2. Perform the titration as described in Part C. Record the pH at the half-equivalence point and the volume and pH at the equivalence point. Save your data files and print out copies of each titration curve for each partner’s lab book and lab report.
3. Analyze your data as described in Part C using the exact calibrated volume of the auto-pipettor. A standard deviation cannot be determined with only two trials. Use the difference of the two trials instead of the standard deviation. The precision based on this range should be better than or equal to 2.0%.
4. At the end of the lab, pump at least 120 pulses of deionized water through the titration pump. NaOH solutions are corrosive and can cause the piston to freeze if left in the pump.
5. Make sure that you keep your NaOH for next week. Label your standardized NaOH with your names, lab section, and standardized Molarity.

Report: Use the report form for this experiment. The information required is listed on the report form. No “formal” written report is required.

In the report form you will: report the average volume delivered in each pulse of the automated titration pump and the standard deviation of the trials. Provide a table containing the results of each standardization titration that you completed; include the mass of KHP, moles of KHP, the volume of titrant to reach the equivalence point, and the calculated NaOH concentration. Include all titrations. Indicate any titrations that were excluded because of student
error or by Q-test. Give the average concentration of your standardized base and the standard deviation of the trials. Report the average and standard deviation of the trials for the auto-pipettor. Provide plots of each titration curve for the weak acid titrations. Give the student name for each trial, the volume of weak acid titrated, the volumes at the equivalence point, and the corresponding weak acid concentrations in tabular form. Report the average and use the range as the uncertainty in the form “the average concentration of the weak acid was average ± range M.” Report the pK_a for both titrations, the average pK_a, and the range (using the format average ± range). The figure captions should list the student who did the titration. The captions on the figures can be hand written. Report all values with appropriate units.

In replacement of a formal discussion you will:
(a). **Consider factors that influenced the precision and accuracy of the data:**
   i. **Give the measurement that is the predominant source of random error for the concentration of the weak acid:** Which experimental measurement, the concentration of the standardized NaOH, the volume of the weak acid, the volume delivered by the titration pump, or the pH gives the largest contribution to the random error in the final weak acid concentration? Note that the best possible precision is equal to the titration pump pulse volume. You cannot determine the volume at the equivalence point more precisely than the volume of a single pulse.
   ii. **Give a source of systematic error in the concentration of the weak acid:** Give a suggestion for a source of systematic error. Make your choice from the calibration of the auto-pipettor, the titration pump, or the pH electrode. Assuming the calibration error is positive (too large), does this systematic error make the final concentration too low or too high? Student mistakes are not systematic errors, they are just mistakes. Systematic errors are consistent for each trial.
(b). **Answer the following question:** Calculate the theoretical pH at the equivalence point of your weak acid using the pK_a and concentration of your weak acid. Compare this theoretical value to the experimentally determined value of the pH at the equivalence point.

Attach copies of your two weak acid titration curves with captions giving the student who did the titration.